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14. ABSTRACT

This report summarizes the different experiments performed in the Universidad Autonoma de Ciudad Juarez (UACJ) and the University of Texas at El Paso (UTEP) to begin a new line of study for our community in radar materials. Radars require materials that have high diffraction coefficient (n) and they need to be electrically insulating at the same time. The current research was inspired by our sponsor: the Army Research Laboratories (ARL) and it is a joint project of the border universities of UTEP and UACJ. This study has two lines of study, the first consisting on deposition of BZN thin film deposition through chemical bath deposition via spin coat, and its characterization developed by UACJ. The second line of investigation is conducted by UTEP and it focuses on BZN deposition and characterization of RF sputtered thin films.

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Cd. Juárez, Chih., December 6, 2010

Project Title

"*Development of Enhanced Performance Tunable RF Materials and Devices For On The Move (OTM) Communications Systems*"

Final Report

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Introduction

This report summarizes the different experiments performed in the Universidad Autonoma de Ciudad Juarez (UACJ) and the University of Texas at El Paso (UTEP) to begin a new line of study for our community in radar materials. Radars require materials that have high diffraction coefficient (n) and they need to be insulating at the same time. The current research was inspired by our sponsor: the Army Research Laboratories (ARL) and it is a joint project of the border universities of UTEP and UACJ. This study has two lines of study, the first consisting on deposition of BZN thin film deposition through chemical bath deposition via spin coat, and its characterization developed by UACJ. The second line of investigation is conducted by UTEP and it focuses on BZN deposition and characterization of RF sputtered thin films. Below are the results obtained at UACJ and UTEP.

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1 Bismuth Zinc Niobate (BZN) film development by spin coating,

1.1 Experimental

The initial reagents to develop this film were bismuth (III) oxide (CAS 1304-46-3), zinc acetate dehydrate (CAS5970-45-6), and niobium chloride (CAS100-26-12).

The first step involved dissolving niobium chloride in water and precipitation of Nb(OH)5 by adding NH4OH. After filtration, the niobium hydroxide was dissolved in an aqueous solution of citric acid (CA) to form niobium citrate (molar ratio CA/Nb=3).

Stoichiometric amounts of zinc acetate and bismuth(III) oxide were dissolved in an aqueous nitric acid solution (50 v/v%), were added to the niobium citrate solution, then the solution was heated at 60 C to form a (Zn, Nb, Bi) complex precursor. Citric Acid (CA) was added to maintain the molar ratio CA/metal=3.

The pH was adjusted to 8–9 with ethylenediamine. Ethylene glycol was added to this solution to promote polymerization of the mixed citrate. In this procedure, the citric acid/ethylene glycol ratio (CA/EG, mass ratio) was 60/40.The resin was kept on a hot plate at 80 C until a viscous gel was obtained.

The resin fluid was deposited onto the substrate surface using static and dynamic dispense, in the first one the resin fluid was under agitation (500 rpm), before the speed was increased at 1900 rpm; the wafer was dried at 100 °C.

The organic phases were eliminated by a thermal treatment at 300 °C for 4 hr in a furnace. Finally the wafer was keep for 2 to 7 hours at 900 °C in order to complete the crystallization process.

1. 2 Results and discussion

1.2.1 BZN film in silicon wafers

The X-ray microanalysis of the polished area confirms the formation of the BZN film onto the silicon wafers. The average thickness of the BZN film was 0.45 mm, however the resulting film was not very homogeneous film.

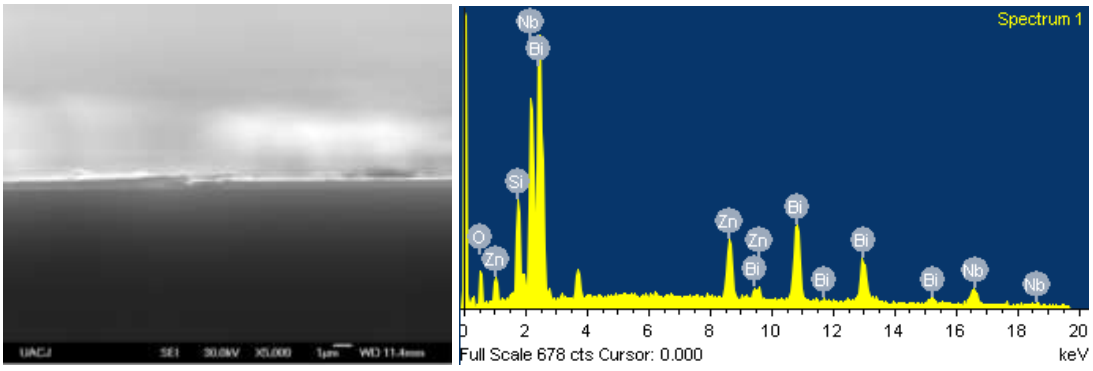

Figure 1. X-ray Microanalysis of the polished BZN film deposited onto silicon wafers.

Figure 2 show the X-ray diffraction pattern of the deposited material in silicon wafer using both static and dynamic dispensed methods. In the dynamic method a $Bi_{1.5}Zn_{0.76}Nb_{1.51}O_{6.8}$, Bi_2O_3 , ZnO phases were found. In the static dispensed method the diffraction peak of the Bi_2O_3, ZnO phases disappear. The big peak at $2\Theta=62$ is due to the silicon wafer.

The SEM images of the deposited wafer by the static dispensed method are shown in figure 3. The Electron Back Scattering images shown that BZN phase material resulted in a fiber shape growth and not homogenous because only 38% of the area has this material shape.

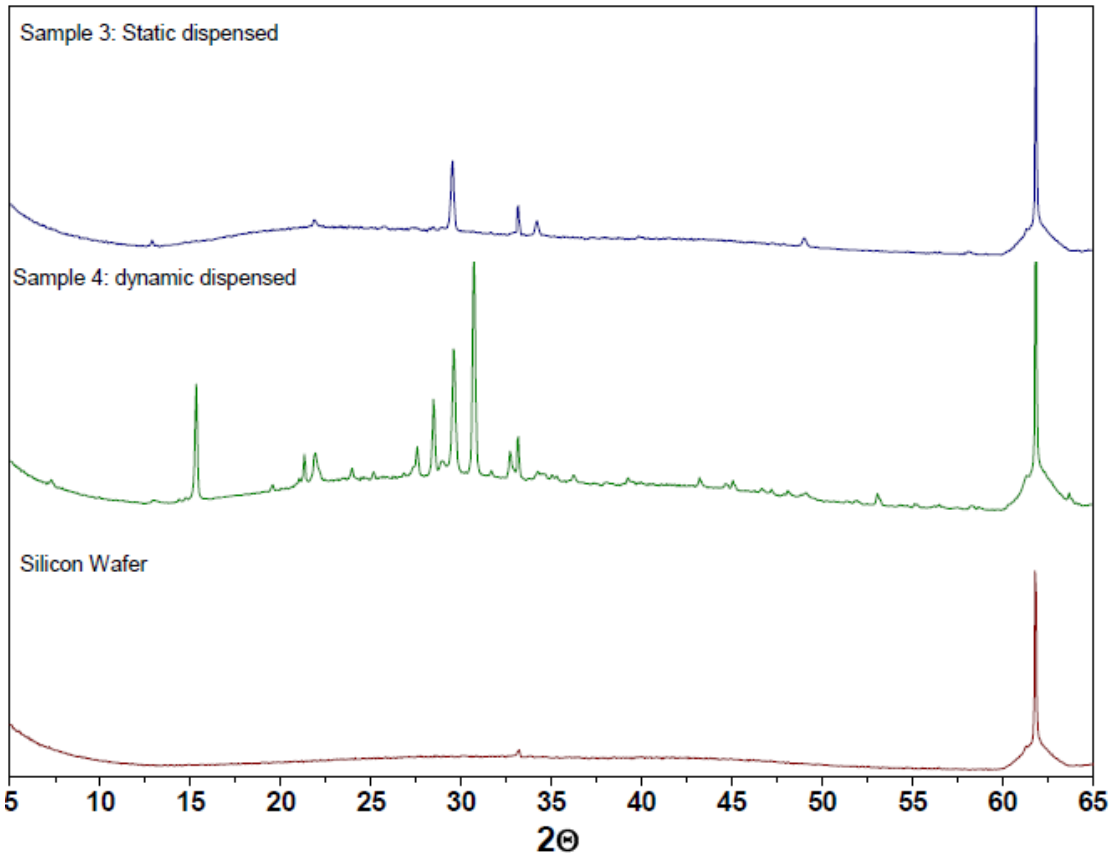

Figure 2. X-ray diffraction pattern of static and dynamic dispensed onto silicon wafer.

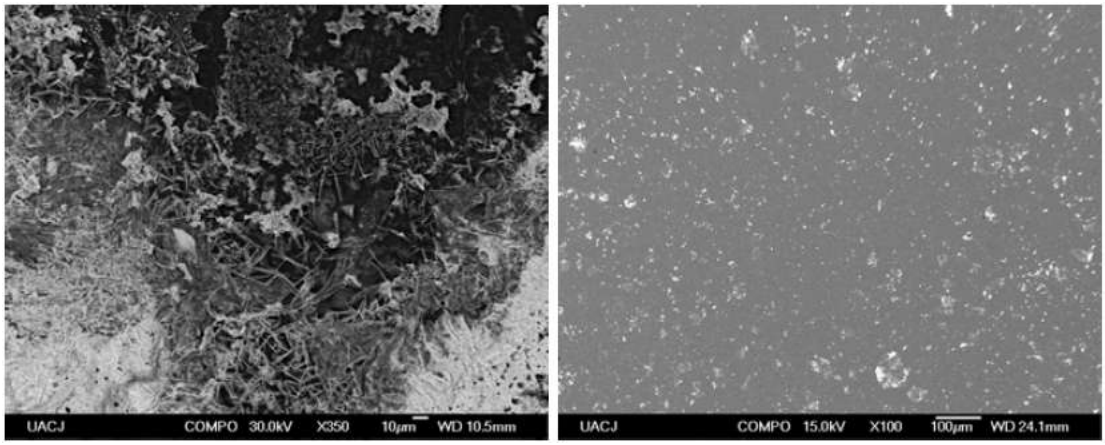

Figure 3. SEM images of deposited wafer using static deposition method.

In the case of dynamic deposition method the 63.8% of the silicon wafer have the growth material (figure 4). Figure 5 shows the elemental distribution on silicon wafers.

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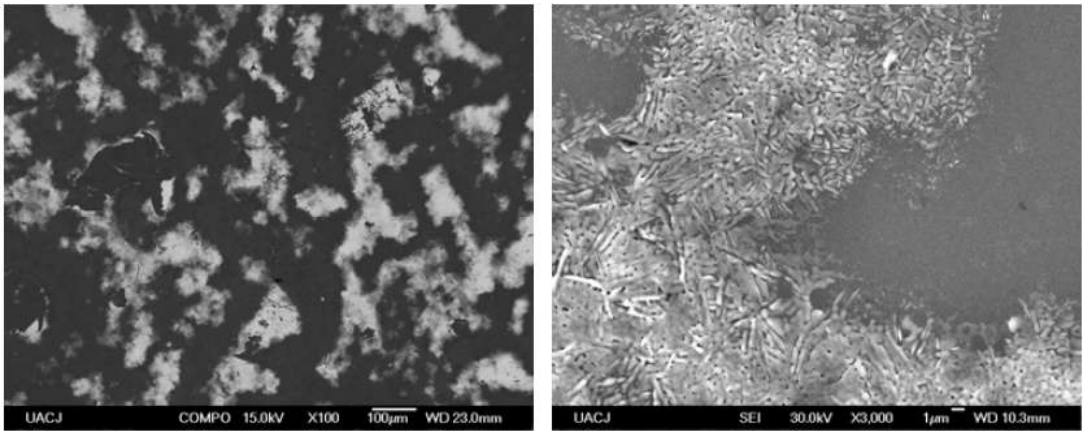

Figure 4. SEM images of deposited wafer using dynamic deposition method.

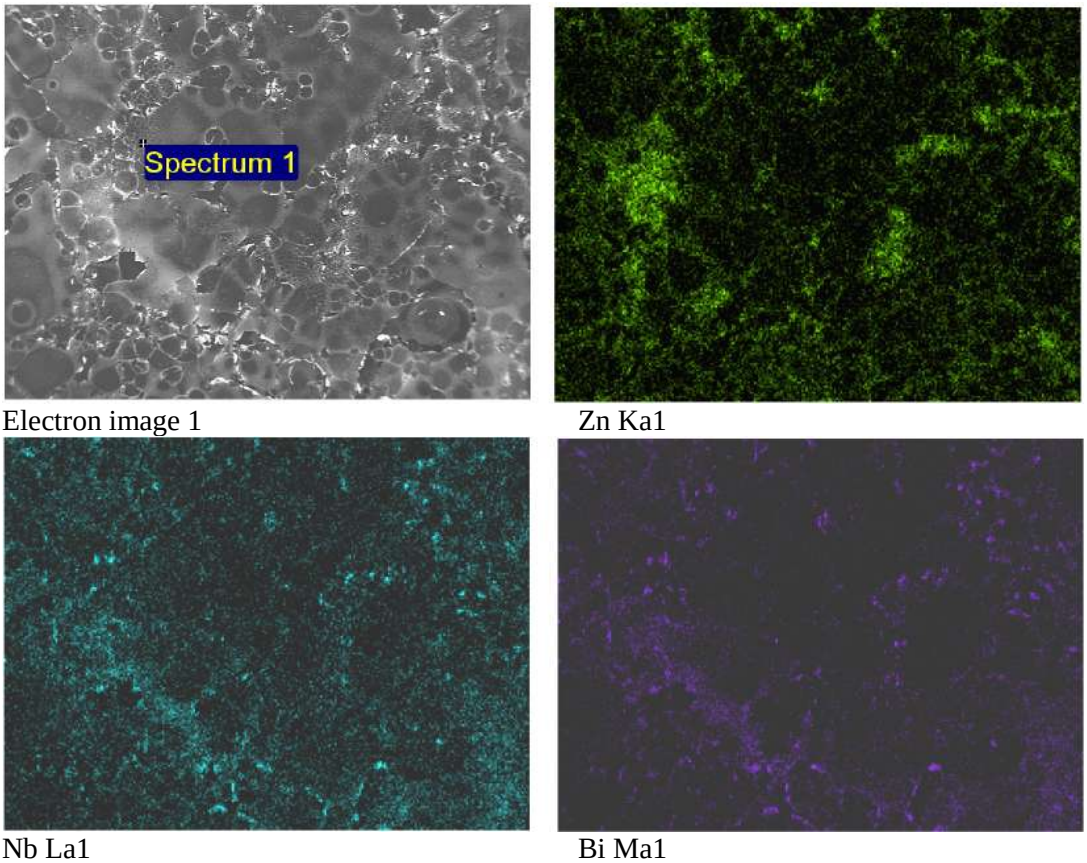

Figure 5. Elemental distribution on silicon wafers.

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1.2.2 BZN film on sapphire wafers

The average thickness of the BZN film deposition was 1.45µ, however the homogeneity it is not consistent. The X-ray Microanalysis of the polished area confirms the formation of the BZN film onto sapphire wafers.

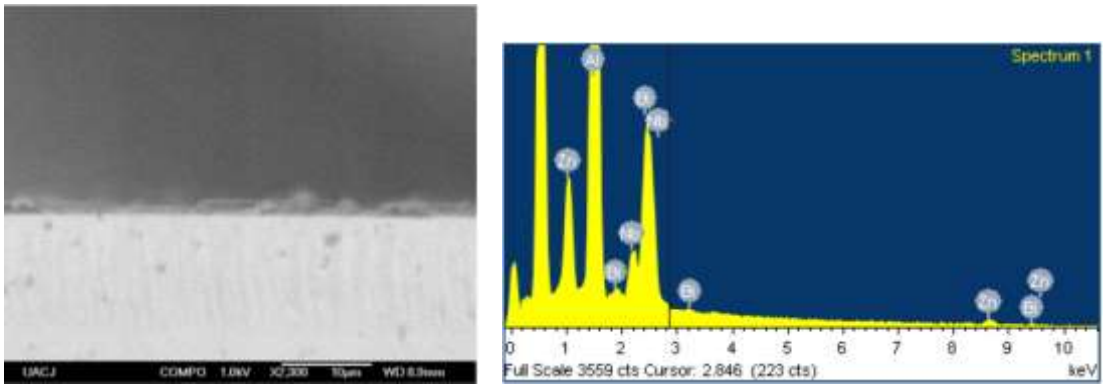

Figure 6. X-ray Microanalysis of the polished BZN film deposited onto sapphire wafers.

Figure 7 shows the growth material onto sapphire wafers. The maximum coated area on the wafer was calculated by diffraction pattern (figure 8), having at 89% of the sapphire wafer coated with the BZN phase. Bismuth zinc oxide and zinc niobium oxide were found as secondary phases. The DRX pattern shows a big peak at 41.7 attributed to the sapphire. Figure 9 shows the elemental distribution on the sapphire wafers, the Zn has a weak signal.

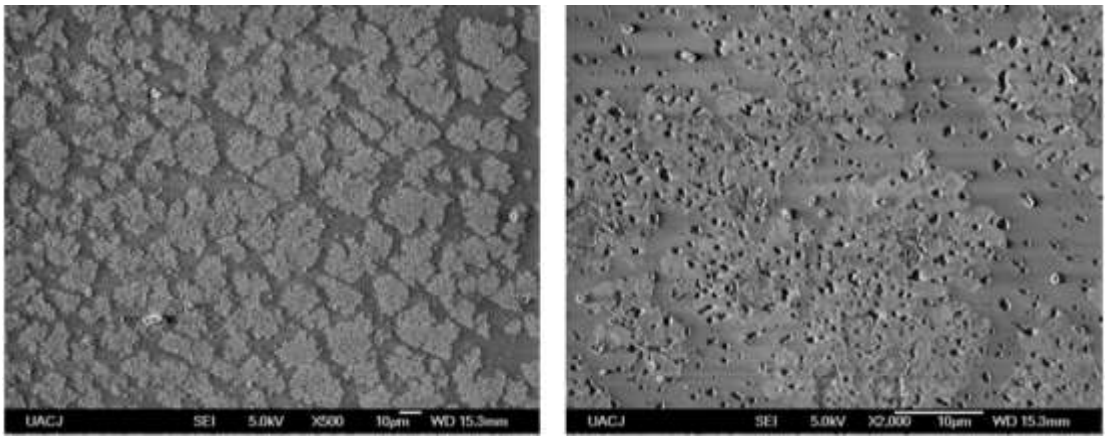

Figure 7. SEM images of deposited material onto sapphire wafer.

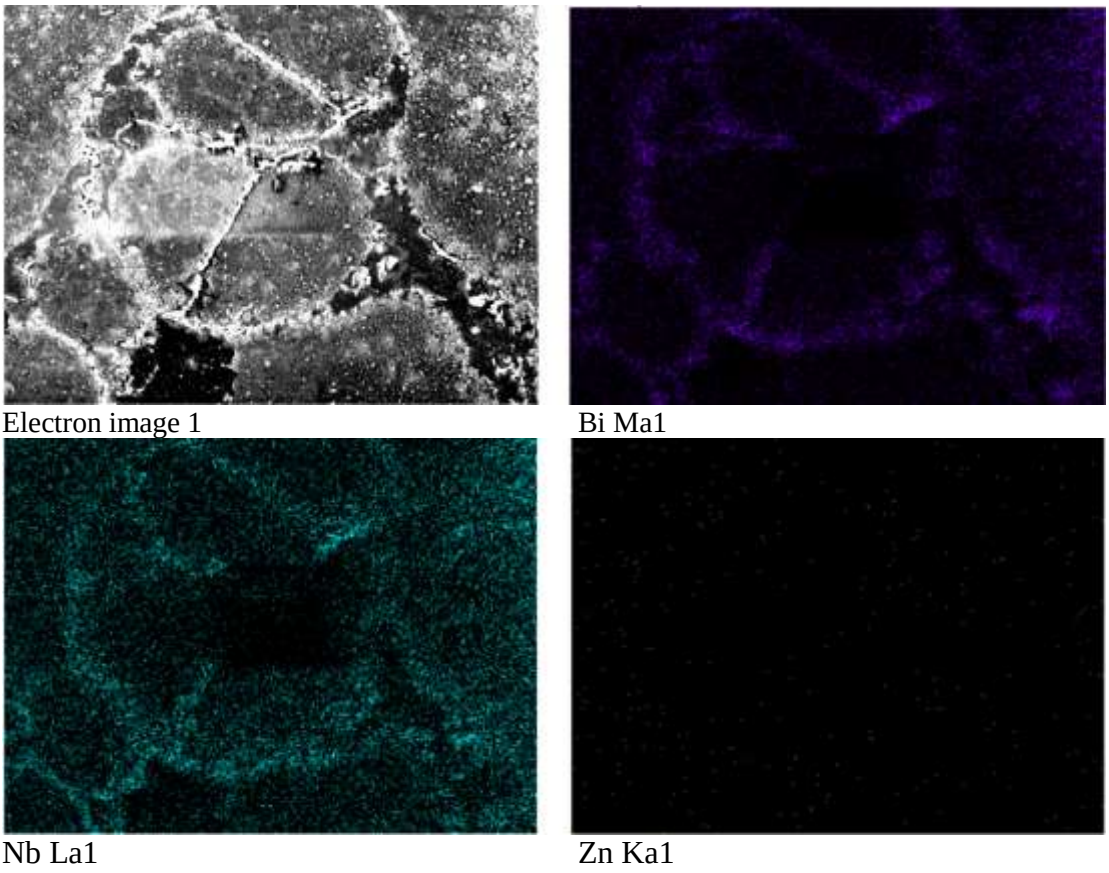

Figure 9. Elemental distribution on sapphire wafers.

1.3 Conclusions on BZN deposition via spin coat

• BZN films were grown in a silicon and sapphire wafers, and where 63.8% and 89% of wafer area was coated by the BZN, respectively.

• In silicon wafers, the particle of BZN has fiber shape growing structures but in the sapphire wafers the particle have semi spherical shape.

• To increase the coated area of the wafers it is necessary to run more experiments in order to optimize the relation between CA and the metallic ions.

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2 Bismuth Zinc Niobate (BZN) film development by Sputtering,

The depositions of BZN via RF sputtering were obtained using a Kurt J. Lesker high vacuum system with capabilities for a 3 inch target of Bi_2O_3-ZnO-Nb_2O_5 (1.5:1.0:1.5, from Kurt J. Lesker). In order to use appropriate parameters for depositions, literature was consulted and it was decided to use power of 50W and 30W. Two samples were grown using the set powers (30W and 50W) for different times: five, ten, twenty and forty minutes. The argon flow used for the 50W BZN thin films was, while the 30W deposition used 24.8ccm of argon.

Table 1 below provides a summary of the different samples with their conditions and corresponding thicknesses using a KLA tencor profiler. Comparable deposition pressures of 1.2 mTorr were observed for both depositions. Morphology of the deposition was also studied and it can be observed in the SEM picture of figure 1.

Table1. - Conditions for BZN sample depositions

Sample	Power	Dep. Time	Dep Press	Ar Flow	Reflective Power	Thickness	Min	Max
x1	50w	10 min	1.2mTorr	20ccm	0	59nm	34.48nm	78.56nm
x2	50w	40 min	1.2mTorr	20ccm	0	211nm	180.59nm	225.06nm
x3	50w	5 min	1.2mTorr	20ccm	0	49nm	18.58nm	75.68nm
x4	50w	5 min	1.2mTorr	20ccm	0	49nm	18.58nm	75.68nm
x5	50w	10 min	1.2mTorr	20ccm	0	59nm	34.48nm	78.56nm
x6	50w	40 min	1.2mTorr	20ccm	0	211nm	180.59nm	225.06nm
x7	50w	20 min	1.2mTorr	20ccm	0	89nm	74.76nm	106.62nm
x8	50w	20 min	1.2mTorr	20ccm	0	89nm	74.76nm	106.62nm
x9	30w	5 min	1.2mTorr	24.8ccm	0	31nm	N/A	N/A
x10	30w	5 min	1.2mTorr	24.8ccm	0	31nm	N/A	N/A
x11	30w	5 min	1.2mTorr	24.8ccm	0	31nm	N/A	N/A
x12	30w	5 min	1.2mTorr	24.8ccm	0	31nm	N/A	N/A
x13	30w	10 min	1.2mTorr	24.8ccm	0	36nm	N/A	N/A
x14	30w	10 min	1.2mTorr	24.8ccm	0	36nm	N/A	N/A
x15	30w	10 min	1.2mTorr	24.8ccm	0	36nm	N/A	N/A
x16	30w	10 min	1.2mTorr	24.8ccm	0	36nm	N/A	N/A
x17	30w	40 min	1.2mTorr	24.8ccm	0	117nm	N/A	N/A
x18	30w	40 min	1.2mTorr	24.8ccm	0	117nm	N/A	N/A
x19	30w	40 min	1.2mTorr	24.8ccm	0	117nm	N/A	N/A
x20	30w	40 min	1.2mTorr	24.8ccm	0	117nm	N/A	N/A
x21	30w	30 min	1.2mTorr	24.8ccm	0	95nm	N/A	N/A
x22	30w	30 min	1.2mTorr	24.8ccm	0	95nm	N/A	N/A
x23	30w	30 min	1.2mTorr	24.8ccm	0	95nm	N/A	N/A
x24	30w	30 min	1.2mTorr	24.8ccm	0	95nm	N/A	N/A

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2.1 Sputter Depositions

The depositions of BZN via RF sputtering were obtained using a Kurt J. Lesker high vacuum system with capabilities for a 3 inch target of BZN. In order to use appropriate parameters for depositions, literature was consulted and it was decided to use power of 50W and 30W. Two samples were grown using the set powers (30W and 50W) for different times: five, ten, twenty and forty minutes. The argon flow used for the 50W BZN thin films was, while the 30W deposition used 24.8ccm of argon. Table 1 below provides a summary of the different samples with their conditions and corresponding thicknesses using a KLA tencor profiler. Comparable deposition pressures of 1.2 mTorr were observed for both depositions. Morphology of the deposition was also studied and it can be observed in the SEM picture of figure 10.

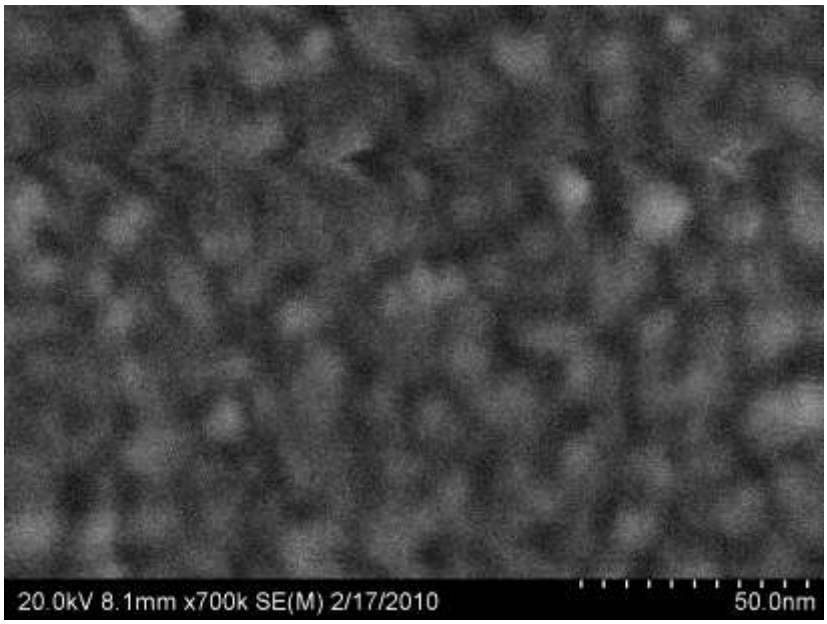

Figure 10.- SEM image of sample X17.

2.2 Elemental Characterization

One of the challenges faced for this line of investigation is optical and elemental characterizations of the deposited films. The approach taken to obtain insight in the composition of the film was through EDS. The spectrums for the eight characteristic depositions were obtained using this method. The spectrum for the sample X24 (Figure 11) is shown below containing Bismuth, Oxygen, Niobium and Zinc along with other elements like the highest peak: silicon; which comes from the substrate. Once all the spectra were collected, a matlab code was used to obtain a firsthand comparison of the atomic weight. Figures three and four correspond to the moles by elements using the EDS counts. Figures five and six are the atomic ratios normalized over Bismuth. Table 2 summarizes the atomic composition on the film normalized over the target composition. As it can be observed, zinc was prominently high through all the depositions.

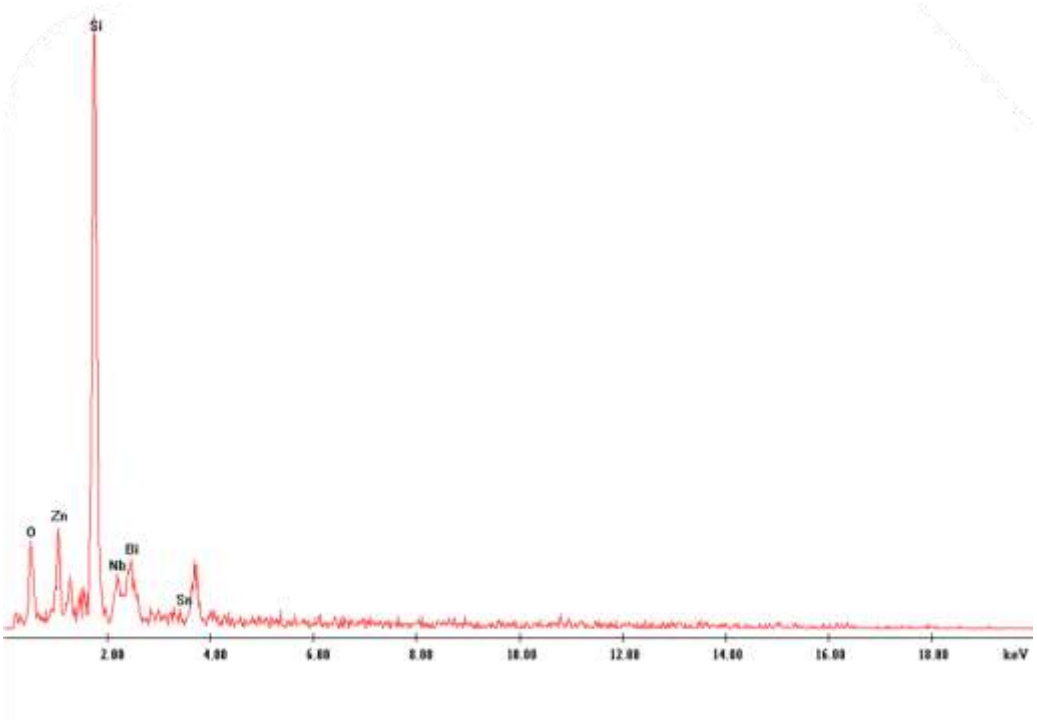

Figure 11. EDS for sample X24.

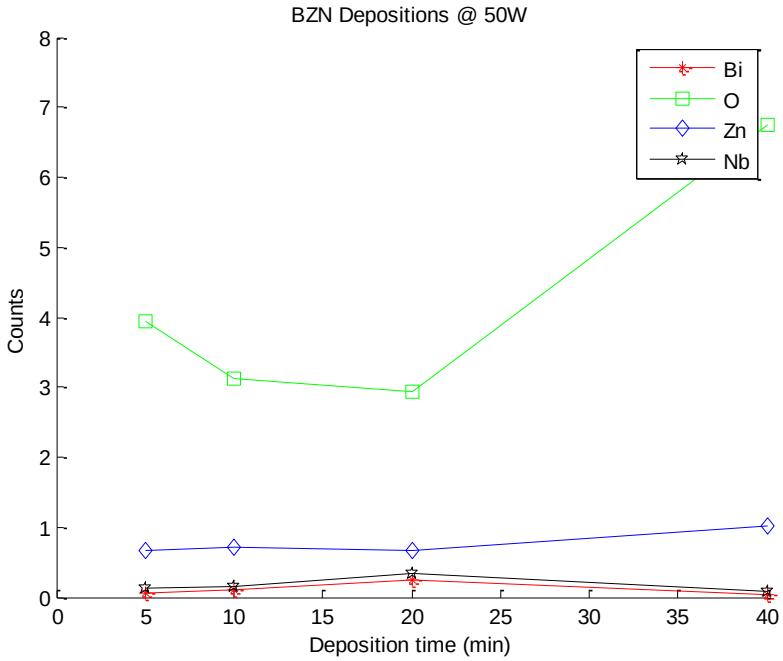

Figure 12. Atomic counts by elements for depositions at 50W.

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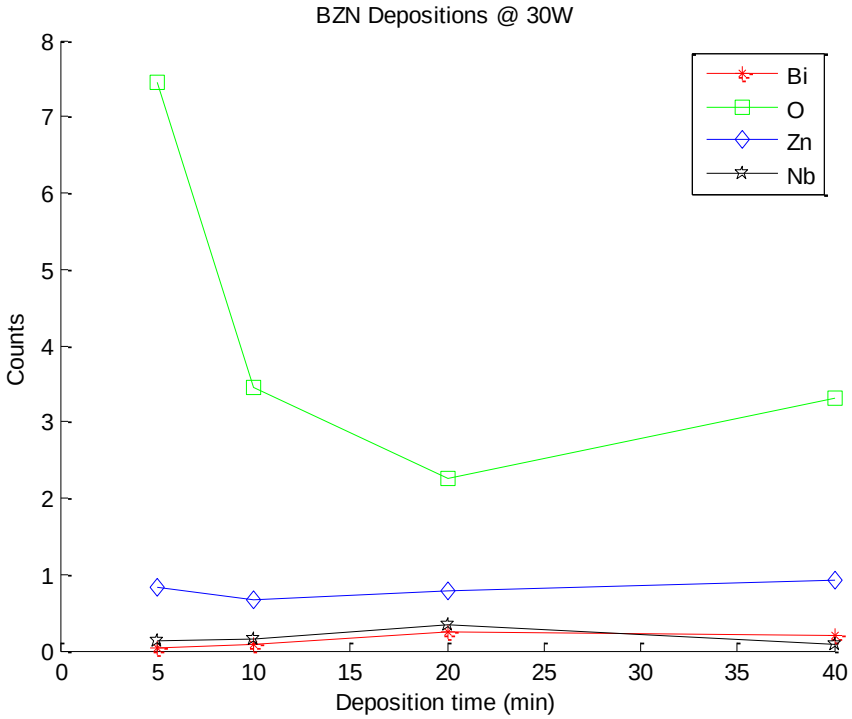

Figure 13. Atomic counts by elements for depositions at 30W.

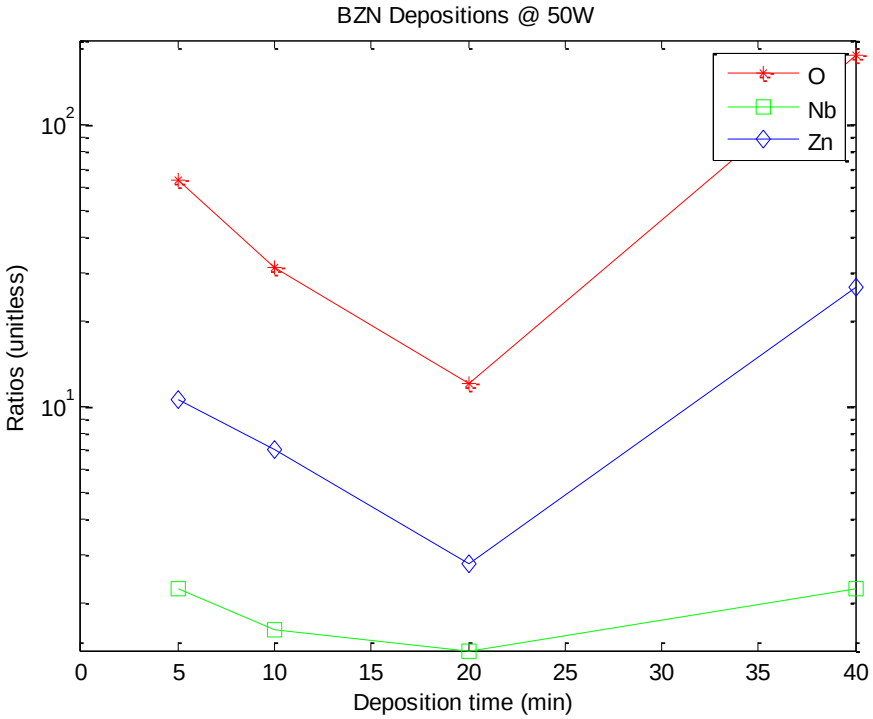

Figure 14. Atomic ratios normalized by Bismuth for depositions at 50W.

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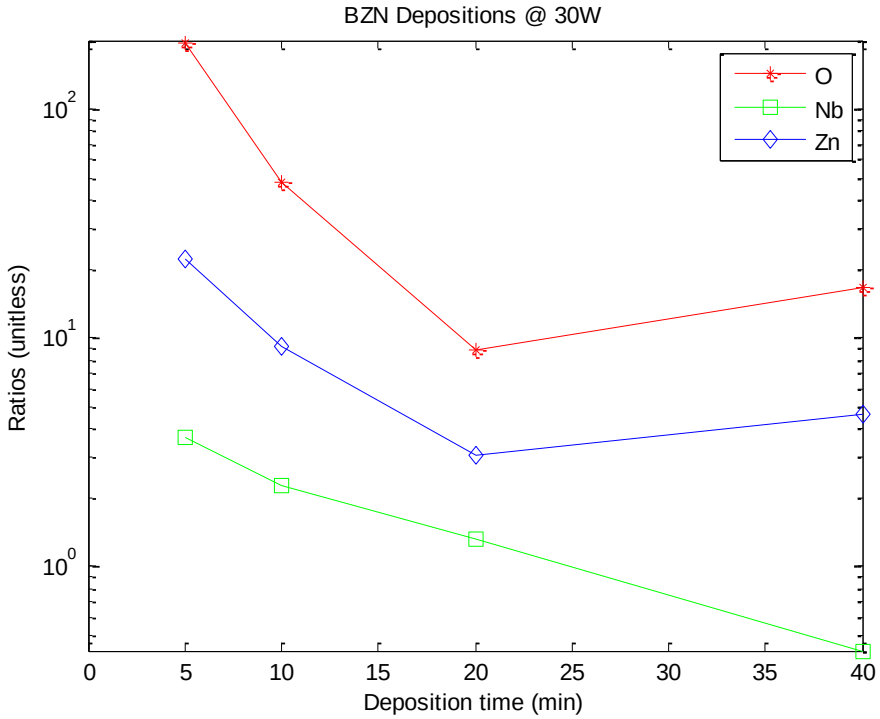

Figure 15. Atomic ratios normalized by Bismuth for depositions at 30.

Table 2. Composition ratios compared to original target compositions.

Deposited/Original				
Compounds		Bi2O3	ZnO	NbO5
Original Composition		1.5	1	1.5
	Time (min)	O/Bi	Zn/Bi	Nb/Bi
50W	5	14.72574	32.03848	2.2494
	10	7.23486	21.21697	1.6067
	20	2.800326	8.356667	1.3673
	40	41.02172	79.91	2.2494
30W	5	45.19986	66.59152	3.6522
	10	11.14023	27.76667	2.2494
	20	2.063977	9.320606	1.3157
	40	3.834488	14.06788	0.4285

2.3 Optical characterization

Since the application targeted is for radars, another valuable characterization for this research is the study of the optical constants for the films. A major characteristic looked in this material is a high refractive index. Consequently, the reflectance of the different samples were obtained ranging from UV (350 nm) to short infrared (2500nm). The measurements were obtained in a Varian spectophometer Cary 5000 with a nitrogen environment. In order to interpret the data obtained from the Cary 5000, the raw data was manipulated and was then input to software available by another optical characterization company: Filmetrics. FilmMeasure has strong and complete software that allows analyzing the reflectance spectrum. Using the data obtained from the Cary 5000, an estimate of the thicknesses and more importantly the refractive index of the films were obtained. In figure 16, a fit that was obtained by FilmMeasure using a cauchy model can be observed. FilmMeasure has the capability to iterate several thousand times until a good fit is found using a material model and an estimated thickness. Once all the measurements were performed the diffractive Index of refraction for 30W and 50W were plotted using MATLAB to obtain a visual perspective of the diffractive index (figures 17 and 18).

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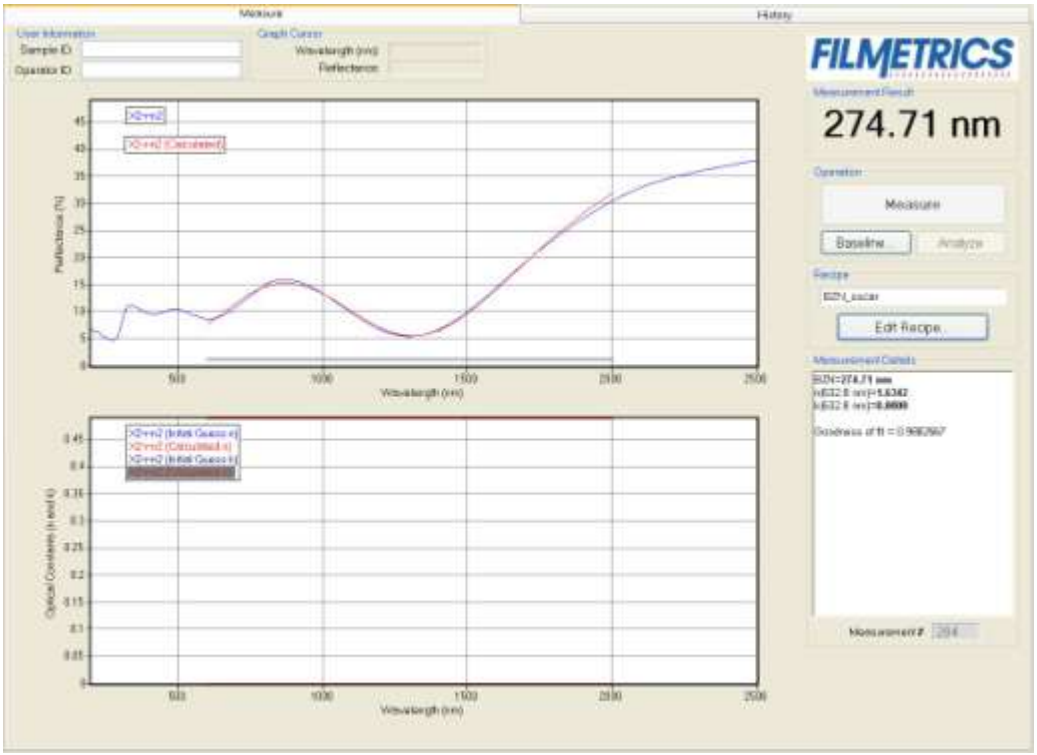

Figure 16. Spectrum for sample X2 (50w for 40 minutes).

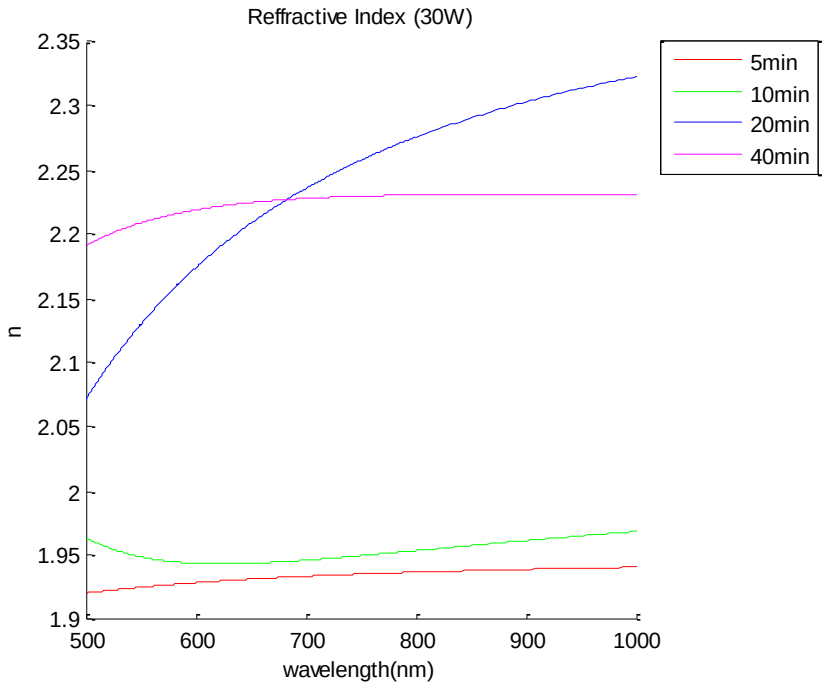

Figure 17. Reffractive index for BZN samples at 30W.

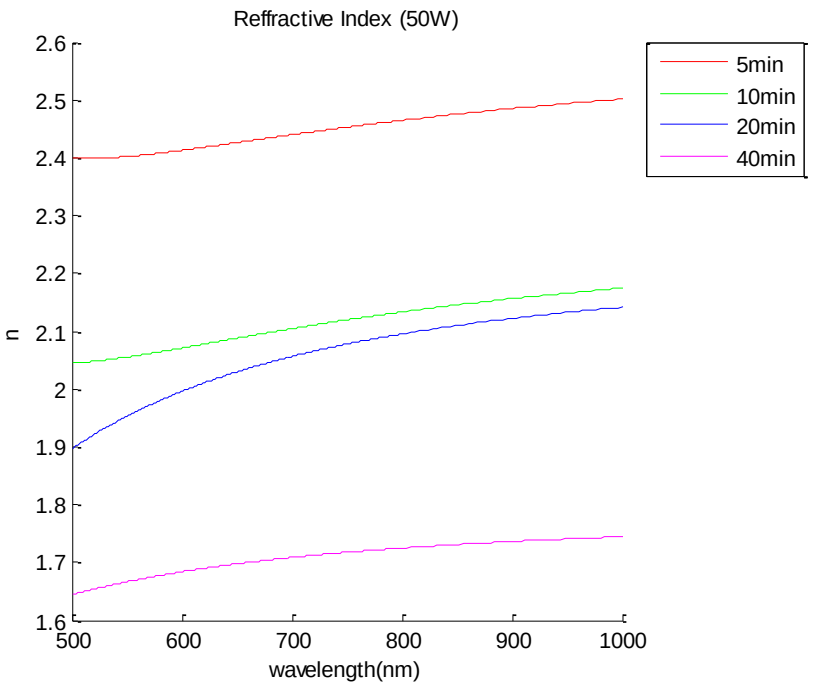

Figure 18. Refractive for samples at 50W.

2.4 Conclusions on Sputter Deposition of BZN

The work performed in the recent months has allowed to face up the task proposed to deliver research in photonic materials like BZN. In summary, it has been shown that deposition of BZN can be grown by RF sputtering. Optical, morphology and elemental characterization has also been achieved thanks to instrumentation like SEM, Filmetrics, Cary 500 and EDS analysis.

In order to obtain the best pursuable results it is important to face several concerns. First, BZN depositions have been obtained, but correct composition is yet to be proven. For this task, it would be important to explore in depth the possibilities that EDS can provide. In case this method does not fulfill, another options like XRD, XPS

and XRF that might be available should be considered. Once the correct composition of target has been found a more robust optical characterization should by executed. Transmittance spectrum must be also obtained to not only obtain the extinction coefficient, but obtain more reliable measurements of the diffractive index. Besides, transmittance and reflectance analyses would allow to obtain the dielectric constant of the material which could also be obtained electrically using CV plots. Once these three areas have been dominated, several runs of deposition varying the plasma or making use of annealing should be made to study their effect on the films.